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THE STRUCTURE OF MATTER

Four Lectures by P. DEBYE
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WITH 21 ILLUSTRATIONS

Translated from the German by
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TRANSLATOR'S NOTE

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ERRATUM

"Potassium ferrocyanide" on p. 65, line 5, should read "calcium ferrocyanide."

FOREWORD

In the last few years I have been asked to deliver lectures in Germany, in England, and in America, on questions concerning structure, which have engaged our interest at the Leipzig Institute. The following four lectures—put out in customary finished form by the firm of S. Hirzel—are my attempt to fulfill the wish which many have expressed, to see the lectures in print in the form in which they were delivered, so that others besides specialists may be able to understand them.

P. DEBYE.

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INVESTIGATION OF MOLECULAR STRUCTURE BY AID OF THE INTERFEROMETER

The wonderful success of the structural formulae of stereochemistry in explaining the chemical behavior of the substances represented, convinces even the physicist that such formulae must indeed exhibit the essential features of the architecture of atomic groups, and encourages the attempt, not only to seek direct proof of the qualitative legitimacy of the formulae, but also to find out quantitative relations by aid of which a true molecular model may be built. The obvious method is to measure the atomic spacing by optical methods, but such methods must be special and must differ from ordinary microscopic methods on account of the extraordinary smallness of the objects observed. In the ordinary microscope visible light is used and this light goes through two processes, namely that of scattering by the object being observed and then of collection by a system of lenses, the lenses being so grouped together that they produce an enlarged image of the object, which is as nearly as possible a true likeness. Abbe emphasized the importance of the error of thinking, chiefly, of the second of these processes and regarding the first as of only minor importance. The lens system can, in fact, correctly reproduce only those details of the object which have influenced in a sufficiently characteristic manner the rays of light sent out in the process of scattering by the object. Now the light ordinarily used has a finite wave length of the order of 1/2000 of a millimeter and when such light is scattered from two spots whose separation is less than this small distance its angular distribution can hardly be distinguished from that of light coming from one single spot. The consequence is that, no matter how practically perfect its lens system may be, the microscope is unable, in such cases, to tell us whether we are observing two points on the object or only one. From this we learn two things, first, that optical methods of measurement must employ light whose wave length equals, or preferably is less than, the smallest distances that have to be observed and, secondly, that the lens system of a microscope is not absolutely necessary to enable an observer to recognize the fine details of a light scattering object. It ought to be possible to find out the details of an object by direct examination of the distribution of the light in the scattered light stream.

Bearing all this in mind we turn back to the consideration of the molecule. The space intervals to be dealt with are of the order of one Angstrom ($=10^{-8}$ cm.) or one five-thousandth of the wave length of visible light, and we have to use invisible light, namely Röntgen rays, whose wave length is of this order. Lenses for rays of such short wave length are not available, but, as we have seen, neither are they necessary.

It is true that we are worse off in two ways than when using ordinary light. What we are able to measure is the relation of the intensity of the scattered light to its angle of scattering (that is to say, the angle between the primary or incident ray and the scattered ray). In the ordinary microscope not only does this angular distribution of intensity take part in the formation of the image but also the relative phase of the rays in the various parts of the light stream. In the case of Röntgen rays, however, it is impossible to measure or use the phase relations. This is the first point. A second difficulty arises from the fact that we have to make measurements upon free molecules. What we have to examine is not the light thrown off by one single molecule at rest, but is that of a restless group, each member of which suffers continuous change of orientation.

The conditions may be analyzed by reference to Fig. 1, in which S is a point (as, for example, a pinhole) sending out the primary light beam and AB is a diatomic molecule from which the incident light is scattered. In order to observe the scattering, a cylindrical photographic film FF encircles the molecule, which lies at the center of the circle.

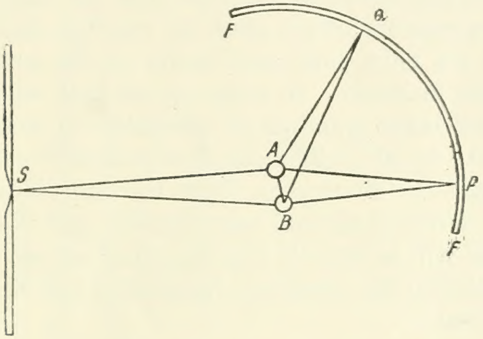

Fig. 1. A diatomic molecule sets up interference.

The path of the primary beam is from S to the point marked P on the film. At P two scattered rays AP and BP come together, one from each of the two atoms. The difference in length between the paths SAP and SBP being negligible compared with either path, it follows that the rays coming together at P are in phase, their amplitudes re-inforce each other, and there is at P a finite light intensity. At such a point, however, as Q, the paths SAQ and SBQ, of rays which come together, are of different lengths, and if, for example, they differ by exactly half a wave length, those rays are in opposite phase. Hence, at Q, the resultant light intensity is nil. Thus there are formed on the film alternate patches of light and darkness, observation of whose angular separation enables us to determine the distance AB in terms of the wave length of the primary light. These conditions would obtain if the molecule AB were fixed in space. Since in fact, however, the molecule assumes, in succession, all possible orientations, it follows that, for each new orientation, there is a new position for, say, the patch, Q, of minimum brightness. One might expect, therefore, that, on the average, interference effects would be wiped out. Careful consideration shows, however, that matters are not so bad as this. The waves of distribution of intensity are indeed blurred—the blurring increasing with the angle between the primary and secondary beams—but calculation demands that the remaining effect shall be readily observable.

What we have just said refers to the scattering due to one single molecule. In every actual case we have to deal with a very large number of particles—a number of the order of 10^{16} to 10^{17}. The simplest tentative assumption to make is that the scattering from the individual molecules will go on without mutual interference and that what will be observed will be exactly like the effect of one single molecule, except that the resultant intensities will be 10^{16} to 10^{17} times as great.

It is by no means obvious that this is to be expected, and, in fact, it is found to occur only in those cases (gases and vapors) in which the mean distances between the molecules are great compared with their dimensions. In experiments with liquids it is to be expected that in addition to the intramolecular interference, intermolecular interference will occur, resulting from regularity in the mutual arrangement of complete molecules. The problem of molecular structure may best be attacked by experiments which avoid intermolecular interference, namely by experiments with gases.

Experiments of this sort were first made in 1929 in Leipzig. Using carbon tetrachloride vapor ($C\ Cl_4$) the predicted interference phenomena were actually observed and the mutual distances between the chlorine atoms were calculated.

Accurate determination of structure demands very careful measurement of the intensity of the scattered light in relation to its angular distribution. In order to explain the experimental details I will discuss the simplest possible case, namely, that of a diatomic gas, and will choose chlorine (Cl_2), a gas which, in the meantime, has been examined by Richter.

The simple assumption with which we had worked up to that time was this, that each atom within a molecule may be regarded as a point from which rays of scattered light

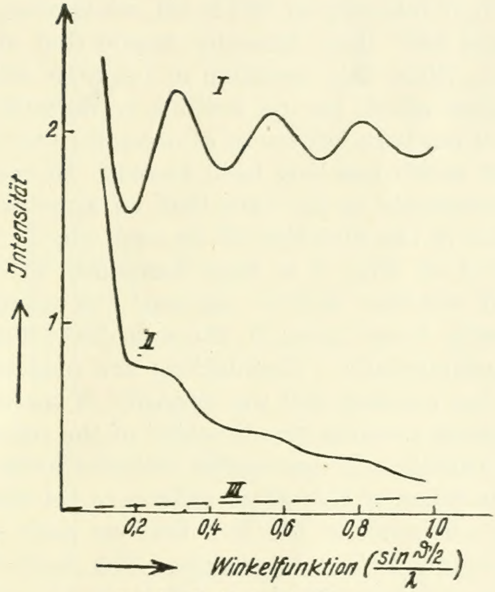

Fig. 2. Scattering in Cl_2.

go out in all directions. Curve I of Fig. 2 indicates the relation which then may be expected between intensity and angle of scatter for a system of two scattering points 2.0 A apart illuminated with radiation having a wave length of 1.54 A. Instead of the angle of scatter, the function $[(\sin \vartheta/2)/\lambda]$ of that angle has been used as the independent variable, ϑ being the angle and λ the wave length of the illumination in Angstrom units. Theory preferred this function.

It should be noted that the curve has been corrected for an effect which occurs in all scatter phenomena, namely, the difference in the scattering of the two polarized components into which the unpolarized primary Röntgen beam may be resolved. The waves which are in a plane perpendicular to that containing the primary and secondary rays, are scattered equally in all directions. Those, however, which lie in that plane are scattered unequally. For example, their intensity at 90° is nil, while along the directions 0° and 180° their intensity equals that of the other component. Since this variation of intensity with angle is a polarization effect, having nothing to do with molecular structure, it has been left out of of account in the curves. It is an effect which has long been known. In radio telegraphy it corresponds to the fact that an antenna sends out no radiation in the direction of its own length.

Curve I of Fig. 2 is that demanded by the "point theory"; it exhibits definite maxima and minima and it differs greatly from Curve II, the data for which were obtained experimentally. Undulations are present but they are much less marked, and the intensity of scattered radiation is greatest towards the direction of the primary beam, falling off rapidly with increasing obliquity away from that beam. The cause of this great difference between curves 1 and II lies obviously in the fact that we have no right to regard the atom as a point source. The scattering of the Röntgen rays is brought about, not by the nucleus, which, being very massive, is too stable, but rather by the less massive electrons whose movement is considerably disturbed by the primary radiation.

The radiation commonly used is that from copper or from molybdenum and has a wave length either of 1.54 or of 0.70 Angstrom units, while the "electron cloud" of an atom under observation occupies a region having dimensions of the order of one Angstrom unit. It is thus clear that in scattering Röntgen rays an atom has no right to be regarded as a point source of negligible dimensions. We must expect, on the contrary, to have to picture the scattering due to one simple atom as itself an interference phenomenon involving the mutual interference of waves of scattered radiation coming from different spots in the electron cloud. The details of such an effect had already been worked out in reference to the atom, regarded as a planetary system of electrons, and the conclusion had been

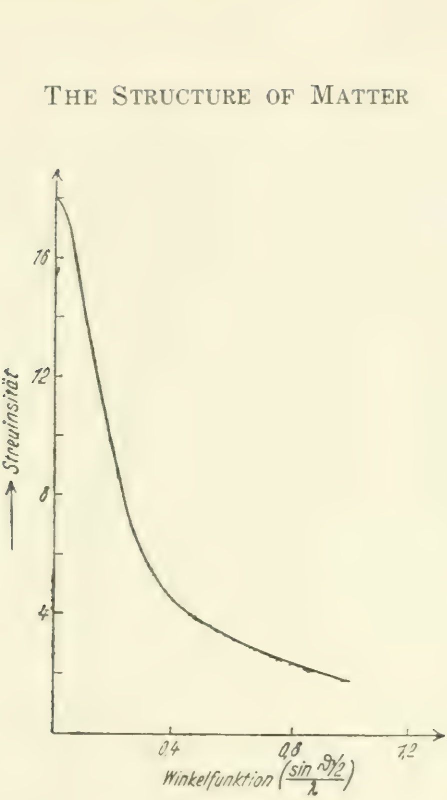

Fig. 3. Scattering in Argon.

reached that observable undulation ought to occur in the intensity curve. Actually no such undulations have been found, but only a continuous falling off of intensity with scatter angle. This is illustrated in Fig. 3, based upon experiments by Wollan and by Herzog on Argon gas. The results are in close agreement with the distribution of electrical charge within the atom demanded by Schrödinger's wave-mechanics. We see, therefore, that the scattering due to single atoms is from every point of view an interference phenomenon, but that on account of the average uniformity of distribution of the electrons, the effect of this phenomenon upon the curve of intensity of scattering is exhibited merely as a continuous smooth falling off of intensity in directions away from that of the primary beam.

With a proper understanding of the curve (Fig. 3) for the single atom the reason becomes clear why Curve II of Fig. 2 rather than Curve I must suit the diatomic molecule (Cl_2) of chlorine. It is true that the discussion of the exact shape of the curve of intensity must make use of an interference calculation which demands a knowledge of the electron distribution within the atom. We are today in the fortunate position of understanding this distribution sufficiently well to be able to work out the angular distribution of atomic scattering. There are two steps in the approximation required. The first is due to Thomas and to Fermi. Their method of approximation, which proves to be very convenient in problems of scattering, provides one single table applicable to all sorts of atoms, for radiation of various wave lengths. There is a closer method of approximation due to Hartree. It is more tedious to work out but it also can be applied by aid of tables—each different atom demanding, however, its own table. A compromise may be made by using a method due to Pauling which, in contrast to Hartree's graphical method, is entirely by calculation.

Assuming that we possess this knowledge of atomic scattering—the "atomic form-factor"—we may now concentrate our attention solely upon the interference due to the relative positions of the atoms within the molecule. An exhaustive discussion demands the consideration of one final correction which, however, is usually small. When atoms are illuminated by radiation of one particular wave length their scattered energy is not confined solely to that wave length. A part of the scattering is of greater wave length. This is the Compton effect. The Compton scattering from the different atoms has, however, no definite phase relation, and the result is that the intensities re-inforce one another but the amplitudes do not. Thus there are no interference effects due to the Compton scattering but there is produced merely a background of intensity which does not undulate but merely increases with increase of angle. Heisenberg has worked out a table by which the Compton scattering may be found for all atoms and for the required range of wave lengths. The correction required by the Compton scattering is small, especially in the case of the heavier atoms. The curve of intensity for this "incoherent" radiation is given, for Cl_2, in Curve III of Fig. 2.

In explaining the details of Röntgen ray scattering I have referred to Cl_2 because this diatomic gas forms an example readily understood. The chlorine molecule is not particularly well suited, however, for the demonstration of interference phenomena peculiar to some particular chosen molecule. The two atoms in the chlorine molecule are the smallest possible group in which interference can occur. It is to be expected that much more marked interference maxima may be observable in the case of a molecule of more complex structure. By following out the calculation for molecules of chosen structure the conclusion is reached that interference phenomena may be pictured, in all cases, by the superposition of a number of curves of scattering, namely, as many curves as there are pairs of atoms within the molecule's structure,—that is to say as many curves as it is possible to draw "links" joining one atom with another. For atoms regarded as mere points each such combination gives a curve of scattering like I in Fig. 2, the spacing of whose maxima is the smaller, the greater the separation between the pair of atoms. In addition, the bearing of the atomic form-factor upon the size of the atoms must be taken into account. Theoretically this may be done by multiplying the ordinates of the curves obtained for the atoms regarded as points, by the product of the atomic form-factors of the pair of atoms forming the extremities of the links.

The atomic form-factor is great for an atom containing a large number of electrons. In fact, for small angles, it can be set equal to the number of the electrons. Obviously, therefore, we may divide the links within a molecule into groups of varying importance. Links joining pairs of atoms, both of which are of high atomic weight, are the most important; those joining pairs of which one member is a light atom and the other heavy, are of less importance. A link loaded at each end with a light atom is comparatively unimportant. From this point of view it seemed to me that the carbon tetrachloride molecule, CCl_4 was especially suitable for preliminary experiments. The mutual separation of the chlorine atoms must have great influence upon the interference phenomena, and if, following the theory of van't Hoff, we regard the chlorine atoms as occupying the corners of a regular tetrahedron, then these distances of separation are all equal. Thus the interference curves that have to be superimposed are all alike and in the case of CCl_4, we may expect to find well marked maxima and minima in the curve of scattering. Experiments bear this out.

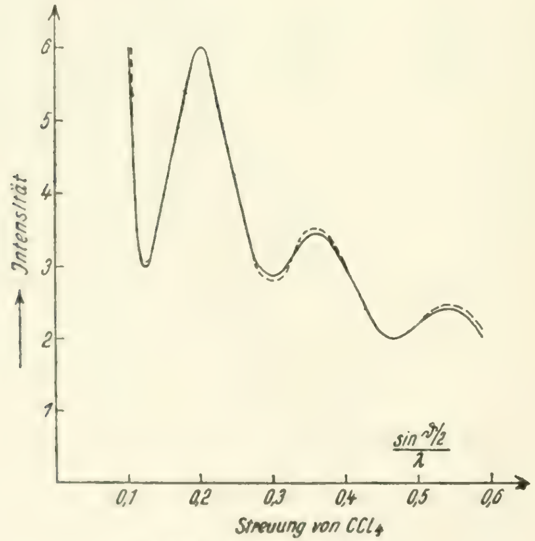

Fig. 1. Scattering in CCl_4.

The consideration of this case is helped by reference to Fig. 1, the curve of scattering for CCl_4 obtained by van der Grinten, who made his experiments with very great care. Instead of employing the usual imperfect filters to ensure the accuracy of the wave length of the primary light beam, van der Grinten obtained mono-chromatic light by reflection from a crystal of rock-salt. The method involves considerable loss of energy, and since, in any case, the scattering in CCl_4 vapor is of small intensity, relatively long exposures (some twenty hours) had to be used.

The object was to obtain, with maximum possible precision, an experimental curve of intensity distribution for comparison with the curve predicted theoretically. The dotted curve in Fig. 4 is the theoretical curve, and it falls remarkably close to the full-line curve which records the actual experimental data. The inference is not only that the theory of tetrahedral grouping is warranted, but also that our notions about the electron distribution within the atom and about the atomic form-factor are sound.

During these experiments the attempt was made to find out whether temperature has any marked effect upon the intensity of the scattering. Theoretically there must be such an effect since at higher temperature the atoms must vibrate within the molecule with increased amplitudes. This must effect an increase in the size of the "electron cloud" and a consequent change in the value of the atomic form-factor. Practically, however, any such temperature effect was too small for observation—as indeed the theoretical calculations of James had predicted. It seems that the atoms within the molecules of organic substances are bound together so rigidly that their thermal excitation has no marked influence upon the curve of scattering.

Even in the case of a substance as well suited as CCl_4 for the observation of interference phenomena, the maxima in the curve of scattering are much broader than those obtained by the use of crystalline substances. Using as primary beam the radiation from copper, the wave length of which is 1.54 A, the first maximum occurs at a scatter angle of 36°, the next at 67° and the third at 110°, the gradients of rising and falling values of intensity filling the whole of the intervening spaces. We must remember, however, that the number of atoms is in this case only four, whilst in a crystal whose three dimensions are of the order of one-tenth of the wave length we must expect—in accordance with such dimensions—the number of particles taking part in the phenomenon to be of the order of a million. The question with what accuracy, under such a handicap, the atomic spacing in CCl_4 can actually be estimated, may be answered by reference to the following table due to Bewilogua:

TABLE

	Angle in degrees	Spacing in Angstroms
First minimum	23.5°	3.00
First maximum	36.0°	2.97
Second minimum	55.5°	2.98
Second maximum	66.5°	3.01
Third minimum	93.5°	3.00
Third maximum	110°	2.96

Here, from six angle measurements, six values are obtained for the spacing of the chlorine atoms, and we may reasonably conclude that the average of the six values, namely 2.99 Angstroms, must be accurate within ± 1%.

The success of such interference experiments, using Röntgen rays, led Mark and Wierl to seek corresponding results with cathode rays. It is true that cathode rays are streams of electrons, but de Broglie has shown that beams of material particles may be refracted like beams of light and do actually exhibit interference. According to de Broglie they behave like light beams of wave length $\lambda = h/mv$, where m is the mass of each particle, v its velocity and h is Planck's constant. Thus the wave length corresponding to cathode rays accelerated by a potential difference of 30,000 volts is about 0.07 A, and the passage of such rays through, say, the vapor of CCl_4, should, as in the case of Rontgen rays, provide a curve of scattering having maxima and minima, in which, however, the 20 to 1 reduction in wave length ought to reduce, in the same proportion, the angular spacing of the peaks. Such predictions are, in fact, borne out by these beautiful experiments. The beam of cathode rays, in its high-vacuum chamber, passes at right angles through the stream of vapor—which is then immediately condensed again to liquid by impinging upon a wall cooled by liquid air— and falls, at an appropriate distance, upon a photographic plate. This plate is perpendicular to the cathode beam and records both the point of entry of the primary beam and the track of the scattered rays.

Cathode rays are much more strongly affected by an atom than Röntgen rays. Roughly this may be explained by the deflection of the atomic nuclei in the electric field, but, in fact, the outer electrons play also an important part in determining the angles of scatter in molecular inteference phenomena. It is the strength of these interactions which gives to cathode rays their marked effectiveness in such experiments. In contrast to the hours required for a photographic exposure when using Röntgen rays, an exposure of but a fraction of a second suffices with cathode rays.

More accurate determination of structure demands a more complete consideration of the distribution of intensity. Reliance must not be placed upon measurement by eye of the diameters of the interference rings—which often seem recognizable clearly as regions of maximum darkness in photos made with cathode rays. By a peculiar physiological effect it may happen that comparatively small changes in the shading of the dark patches may produce an appearance of maxima and minima which is illusory. It is true that, in spite of this difficulty, analyses of structure always have been based upon the measurement of such ring diameters. This does not detract from the validity of the results, but I believe that the exactness of the measurements of intervals has often been overestimated. Nor can the use of the Röntgen ray method of observation be avoided in the future, in cathode ray work, although the difficulties in the latter case are much greater. That the interference bands will be less distinct for cathode rays than for Röntgen rays, is to be expected, because the atomic form-factor for cathode rays falls off more steeply than for Röntgen rays, with increase of angle. It may be found, however, that such loss in detail is compensated by the increased readiness with which interference of higher order may be obtained by means of cathode rays.

In conclusion we will show, by reference to three examples chosen from a large number of structure analyses made by the latest method, what are the conclusions to which such experiments appear to lead.

Bewilogua has examined not only CCl_4 but also the molecules $CHCl_3$ CH_2Cl_2 and CH_3Cl. The object was to find out what changes in structure occur when the number of heavy atoms was reduced successively from 4 to 3, then from 3 to 2 and finally from 2 to one. The trend of the changes is shown by the curves of Fig. 5 based upon Bewilogua's actual data. The blurring of maxima and minima with reduction in the number of the chlorine atoms is evident. If all the atoms except those of chlorine are left out of consideration there remains, in the case of methyl chloride (CH_3Cl), no undulation at all in the curve. Actually the C-Cl pair provides enough interference to put noticeable undulation into the curve. This undulation is particularly interesting because, from its angular position, an estimate can be made of the distance between the carbon atom and the chlorine atom—which, according to the tetrahedron picture, must be the distance from the middle point of the tetrahedron to one of its corners. The value thus estimated agrees well with the tetrahedron picture.

Careful consideration of the other three curves leads to an estimate of the mutual separations of the chlorine atoms. Bewilogua finds a separation of 3A in the case of CCl_4, increasing to 3.1A for $CHCl_3$ and to 3.2A for CH_2 Cl_2. Apparently, therefore, the form of the tetrahedron becomes irregular when atoms at its corners are not all alike, there being mutual repulsion between the chlorine atoms. The work of Wierl corroborates Bewilogua's results for CCl$_4$, using cathode rays, and shows the mutual separations of the chlorine atoms to be equal, but Wierl finds no warrant for the notion that, in the case of other molecules, there is any "stretching" along the valency links. I hear, however, that later experiments made by Dornte in Berkeley (California) do appear to favor such "stretching."

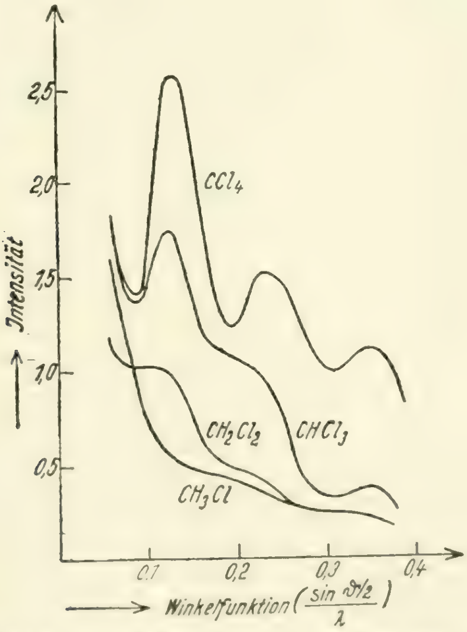

Fig. 5. Scattering in CCl$_4$, CHCl$_3$, CH$_2$Cl$_2$ and CH$_3$Cl.

Another molecule which has been examined both by Röntgen rays and by cathode rays is that of benzene (C$_6$H$_6$). Wierl shows definitely that in this molecule the separation of the carbon atoms is 1.4 A, whilst in aliphatic compounds it is 1.5 A. He has been able to detect definite differences between the diagrams of benzene and of cyclohexane. Extended investigation has been made by Kayser at the Leipzig Institute, of the curves of intensity, using Röntgen rays, for both benzene (C_6H_6) and hexachlorbenzene (C_6H_6). If it is true that the atoms are on the corners of a regular hexagon then there must be three different lengths for the linkages and the curve of scattering must represent the superposition of three curves. Referring to Fig. 6, the first maximum, occurring at the smallest angle, corresponds to the longest interval of separation *a*. The second maximum corresponds to the next smaller interval *b*, but since this interval occurs twice as often as *a*, it follows that the second maximum ought to be more marked than the first. Finally, the third and smallest interval *c*, sets up a third maximum. This does not quite coincide with the second order maximum belonging to the interval *a;* also it is affected to some extent by the curve belonging to *m*. Thus it is to be expected that the third maximum will be broadened out. All these expectations have been corroborated by experiment.

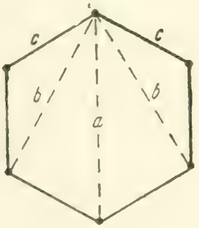

Fig. 6.

Passing from C_6H_6 to the consideration of C_6Cl_6, we expect to find a similar sort of curve of scattering, but one whose maxima occur for smaller angles, because, the chlorine atoms being heavier than those of carbon, the Cl-Cl intervals must naturally be greater than the C-C intervals. This prediction also has been borne out by experiment.

As a final example we may mention dichlorethane (CH_2Cl-CH_2Cl) ; a molecule which is particularly interesting because its two halves should be capable of "free rotation" about the line of the C-C linkage. Such rotation would involve changes in the separation between the chlorine atoms, and since these, on account of their greater content of electrons, are chiefly responsible for the scattering, we may expect our curves of scattering to offer conclusive evidence as to the existence of such "free rotation." The investigation has been made by Wierl, using cathode rays, and by Ehrhard using Röntgen rays. The result, emphasized more especially by Ehrhard, is this: The two halves of the molecule are capable of relative angular shift but not all the possible angular shifts occur equally often. The trans-configuration occurs more often than the cis-configuration.*

It is hoped that the examples we have given may suffice to show that the method of interference forms a valuable aid in attacking problems of structure arising in stereochemistry.

Translator's note: The most familiar cases illustrating *trans-* and *cis-* configuration are those of fumaric acid and maleic acid, both of which have the same formula, but the properties of which are different. The formula of each is $HO_2C \cdot CH{:}CH \cdot CO_2H$ and, to account for the difference in properties, the favored explanation is that there is difference in the configuration of the atoms within the molecules. The configuration proposed for fumaric acid is as in Fig. *a* and is called the *trans*-configuration, while that for maleic acid is as in Fig. *b*, and is called the *cis*-configuration.

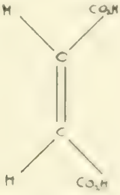

Fig. *b*—Maleic Acid (cis-configuration)

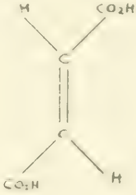

Fig. *a*—Fumaric Acid (trans-configuration)

THE ELECTRICAL STRUCTURE OF MOLECULES

Over a century ago Faraday showed that the capacity of a condenser is increased by the presence of an insulator, a "dielectric," between the plates. By this discovery he laid the foundation for a method which recently has been used in the investigation of molecular structure. The picture used by Faraday as an aid in the understanding of the action of the dielectric may be understood by reference to Fig. 7.

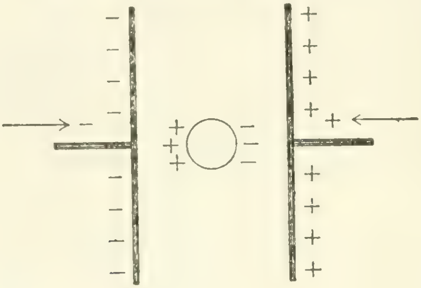

Fig. 7. Increase of capacity by inductive action.

An uncharged ball of metal is introduced into the space between two charged plates. By the inductive action of the plates, the left hand side of the ball now becomes positively and the right hand side negatively charged. These induced charges react upon the plates so as to draw more charge into them. This added charge acts in its turn upon the ball, increasing its induced charges. The ball then reacts further upon the plates, and so the process goes on until a steady "end condition" is reached. The "uncharged" ball has brought about an increase in the charge upon the plates simply because the electricity upon it is movable.

It is hardly surprising that out of such a picture of the phenomenon grew the notion that the molecules of insulators are themselves conducting balls, albeit incapable of transferring electricity from one to another, and that this notion led such men as Mosotti and Clausius to deduce values for the space occupied by the molecular balls, their calculations being based upon Faraday's values of the "dielectric constants," by which the increase in capacity is measured. It is true that the idea of conducting balls has had to be revised, but the mobility of the charges within the molecule is still accepted. In picturing, for example, an undisturbed helium atom as consisting of a heavy positive nucleus and a pair of electrons grouped together as a symmetrical spherical system or cloud of charge, we expect to find that the grouping of the system will be affected by an electric field. Under the effect of such a field the system should become polarized, the nucleus being driven over to one side and the electrons to the other. The effect is indeed very small, for when a helium atom is brought into an electric field of 300 volts per centimeter the shift of the nucleus should amount to only 2×10^{-16} cm., that is to say to less than one hundred millionth of the diameter of the electron cloud. Such minute shifts are, however, sufficient to cause the dielectric constants to deviate considerably from unity—especially in the case of dense dielectrics.

For many decades this explanation has been accepted,—by which an electric field sets up polarity within a molecule by deformation. For the past twenty years, however, I have felt that possibly another effect might be responsible for dielectric action. We know that, when in aqueous solution, HCl, for example, is broken up into ions of hydrogen, carrying positive charge and ions of chlorine carrying negative charge. Now it seems reasonable to suppose that when these ions re-unite to form again molecules of HCl the charges may not again completely interpenetrate, but that the proper picture of the molecule will be one in which there will be an excess of positive charge on the hydrogen side and an excess of negative on the chlorine side, equilibrium being maintained in this condition without the action of an external field. The molecule thus pictured may be called a "polar molecule," its condition representing a sort of preliminary stage in the process towards complete electrolytic dissociation. If indeed such "polar molecules" exist we must expect that the action of an electric field upon the medium will disclose electric properties in it by virtue of the field's directive action, since it will tend to set the positive to negative axes of the molecule into the direction of its own lines of force. From this point of view there are generally two effects which must occur within the molecule, namely, an orientation as well as a deformation.

It would be a distinct step forward in our knowledge of molecular structure to separate these two effects. We could then characterize each molecule quantitatively by its "dipole moment," that is to say by the product of charge and distance apart of a fictitious system consisting of two point charges set over against each other, the electrical molecular field in the neighborhood of which would be exactly like that of the actual molecule.

It happens that a method of separation is available. The amount of orientation imparted to "polar" molecules by an electric field should depend considerably upon their thermal agitation. The higher the temperature, the smaller must be the total orientation produced by a field, and it is to be expected that a gas consisting of polar molecules will have a dielectric constant whose value falls off with increase of temperature—this effect being present even though the gas has been held at constant density so as to ensure the constancy of the number of molecules per unit volume. It proves unnecessary to work out the condition of equilibrium between the organizing effect of the field and the disorganizing effect of the heat agitation. The results were applicable, of the derivation by Langevin, of the Curie temperature law of paramagnetic susceptibility as an equilibrium condition of magnetic moments organized by an electric field. Langevin's results for magnetic moments are applicable directly to the case of electric moments. Careful consideration shows that no account need be taken of the deformation, since this effect, being insensitive to heat agitation, is unaffected by temperature.

Early experiments by Baedeker, made prior to the introduction of the "dipole" explanation, supported by a large number of recent measurements, confirm the notion that molecules can be divided into two large groups. The first group exhibits no temperature effect. It contains the "noble" gases,* diatomic gases such as O_2 or N_2, complex molecules such as CO_2, CS_2, C_6H_6 and also hydrocarbons of the methane series *(Grenzkohlenwasserstoffe)*. Such molecules are exceptional. The great majority of molecules belong to the second group, namely, the group which does exhibit temperature effect. Values of the dipole moments have been found for hundreds of different molecules. Always these are of the order of 10^{-18} electrostatic units—a value which was reasonably to be expected since the charge of an electron is 4.77×10^{-10} E. S. U. and the space intervals within a molecule are of the order of 10^{-8} cm. And it is especially noteworthy that the substances with high dielectric constants are almost always such as have oriented polar molecules. Water, for example, is a typical polar molecule. It has a moment of 1.85×10^{-18}. Ninety-five per cent of its dielectric property is attributable therefore to orientation effect and only 5% to deformation.

In the course of the developments that have occurred during the past ten years, influenced as these have been by Planck's quantum theory, our picture of the conditions of motion of atoms and molecules has greatly changed. For example, in a gas with rotating molecules the rotational energy is not arbitrary and unrestricted as the Langevin theory allowed it to be. The restrictions put upon the rotational movement by the quantum theory when this was in its first stage of development, were deduced first by Bjerrum. The question had then to be considered what bearing the quantum theory might have upon the calculation of the orientation of polar molecules. After some preliminary inves-

**Translator's note:* The "noble" gases are the inactive gases, Helium, Neon, Argon, Krypton, Xenon.

tigations, which were made before the theory had been thrown into its final form by Heisenberg and Schrödinger and have had to be revised, there is general agreement as to the bearing of the quantum theory, in the form of wave-mechanics, upon our problem. We know now that the results deduced from the Langevin theory are quantitatively correct even though both the picture and the method of calculation differ completely from what they were earlier. We may discuss the modern conception by reference to the case of a simple polar molecule, such, for instance, as HCl, consisting of only two atoms. The energy conditions possible for this molecule are definite and distinct. We may assign to them the numbers $n=0$, $n=1$, $n=2$, $n=3$, and so on, and then the amount of energy of the energy level *(Energiestufe)* "n" will be equal to $n\ (n+1)$ times the basic quantity *(Grundenergie)* $(h^2/8\pi^2A)$ where h is Planck's quantum of "action," namely, 6.55×10^{-27} erg-second, and A is the molecule's moment of inertia. This holds only in the absence of disturbing electric fields. In the presence of an external electric field the energy conditions are disturbed. The zero condition or "level" *(Stufe)*, which used to be one of zero energy becomes now a condition of negative energy: the first and all higher levels will be split up into new "component levels" *(Unterstufen)*, of which some represent greater amounts of energy and some smaller amounts than the levels from which they originated. In a gas the molecular energy is distributed among the various levels, those of higher energy being the more sparsely occupied. An increase in temperature causes a wandering of molecules out of the lower levels into the higher. In considering the effective dielectric action of a gas it is, however, unnecessary to worry about the higher levels since, in those cases, the splitting-up process caused by a field happens to be such that the components into which a given "level" is split are so distributed in respect of energy that, on the whole, no change of total energy is effected and the field may be regarded as without effect.

To the zero level, which contains originally all those molecules whose energy of rotation is zero, the action of the field imparts negative energy, that is to say, the molecules in this level become polarized. The sense of the polarity imparted corresponds to an increase in the dielectric constant. In itself this effect upon a zero-level molecule is independent of temperature, but since a rise in temperature causes molecules to wander from the lower to the higher levels, temperature does affect the number of molecules occupying the zero-level. The net result is, therefore, that rise of temperature does reduce the electric reaction of a "polar" gas. Fig. 8 illustrates the energy of the first three stages in the undisturbed and the disturbed conditions.

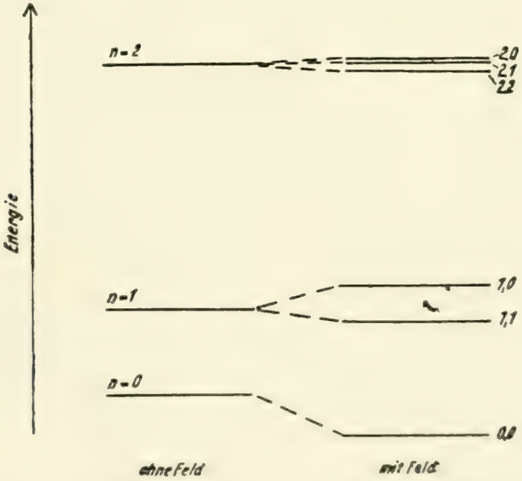

Fig. 8. Splitting up of energy levels in an electric field.

The striking characteristic of the members of the sets of "component levels" in the higher quantum conditions is that some contain less energy and others more than that corresponding to the condition from which the group originated. A molecule which, when subjected to an electric field, suffers a reduction in its energy, behaves in a manner with which we are familiar, namely, when in a non-homogeneous field, it is driven towards the strongest part of that field. It experiences a force of attraction just as a paramagnetic body does when in a non-uniform magnetic field. A molecule, on the other hand, whose energy is increased by the action of an electric field experiences an opposite effect, namely, it tends to go to the weakest part of the field, its action being analogous to that of a diamagnetic body which suffers repulsion by a magnet. Wrede and Estermann have succeeded in demonstrating the peculiar behavior we have just described, by sending a stream of the molecules under investigation, through a non-homogeneous electric field and observing the effect.

A stream of "non-polar" molecules suffered a simple deflection in the direction of increasing field, on account of "deformation," the effect of which is always in the positive sense. In the case of "polar" molecules there is a sidewise deflection in one particular direction upon which, however, is superimposed a broadening towards both sides. The splitting-up of this band into the component streams corresponding to the discrete "levels" of energy promises to be but little instructive and has not yet been done. It is possible, however, to deduce an approximate value for the "dipole-moment" from the amount of the broadening.

The temperature method is very suitable for an exact determination of "polarity," but it has the disadvantage that it is difficult to carry out because the values of the dielectric constants of the gases under consideration differ but little from unity. It would be much easier to experiment upon the gases condensed to liquid, but such measurements would throw no light upon the characteristic molecular constants whose values are being sought. In dense liquids the mutual interaction of the molecules is, in fact, so great that the "association-effects" introduce an extraordinary amount of complication which gets worse with increasing strength of the molecular polarization.

In order to simplify the procedure while at the same time avoiding the disturbing "association-effect," I caused Luise Lange, in 1918, to experiment with dilute solutions of the polar molecules in non-polar solvents. Since that time this method of dilute solutions has been used in a large number of cases and has provided the majority of the values of dipole-moments now known.

Even by this method, however, the result directly obtained is again the sum of deformation and orientation. The method owes its extensive application to a second means, not yet mentioned, of separating the two effects.

While investigating the velocity of propagation of short electrical waves in insulating liquids Drude discovered that, for many liquids, and especially those having high dielectric constants, the propagation exhibited dispersion, the velocity of propagation of the waves falling off for an increase of frequency. For this phenomenon the later dipole theory offered a ready explanation. We saw that when the molecules are "polar" a considerable part of their dielectric action depends upon orientation, that is to say upon rotation of the molecules, and this rotation cannot follow instantaneously upon the setting up of an electric field. A certain time must elapse before equilibrium is reached, and with an alternating field the effect will differ for different frequencies. With low frequency the "relaxation-time" *(Relaxationszeit)* of the orientation will be unimportant, but when the frequency is high, so that the period of oscillation is equal to or actually less than the relaxation-time, the setting of the molecules will respond less and less perfectly. The consequence is that, with sufficiently high frequency, the orientation effect vanishes and deformation alone plays a part. If, therefore, we accompany a low-frequency experiment by one with very high frequency, we must have in the one case orientation and deformation both acting together and in the other case deformation alone, and our measurements will provide a means of separating the two effects

The high-frequency waves actually employed are those of visible light. The use of these makes possible the calculation of the dielectric constants resulting from "deformation" from measurements of refraction, since, according to Maxwell, the dielectric constant is identical with the square of the refractive index.

Briefly therefore. the method consists in examining a dilute solution first with low frequency and then with very high frequency, the dilution being such that "association" effect is negligible. It must be admitted that this dispersion method is not quite as free from objections as is the temperature method, for even the "deformation" component is somewhat dependent on frequency, and it is not easy to find out exactly the amount of this dependence. Also there is a possibility that the dipole-moment may be affected tc some extent by the neighboring non-polar molecules of the solvent. The existence of this latter effect has recently been demonstrated and found to be very small.

We see then that exact measurement of dipole moments by the dispersion method is not possible. In spite of this shortcoming, however, the values of moments found by this method have proved sufficiently accurate in the majority of cases to provide a basis for the discussion of questions of chemical structure. I shall return later to the discussion of the bearing of polarity upon these questions.

According to our dipole theory the anomalous dispersion discovered by Drude must be coupled with the existence of a relaxation time the value of which should be of the order of 10^{-10} second. If we make a rough picture of a polar molecule, treating it as a small sphere of molecular dimensions, the rotation of which is hindered by viscosity, we can estimate the order of magnitude to be expected for the "relaxation time." The conjecture is thus warranted that the anomalous dispersion in the spectrum may be greatly masked *(verlagert)* by change of temperature, since, as is well known, temperature does greatly affect ordinary macroscopically measurable viscosity. Although, obviously, it is daring to derive by extrapolation from macroscopically measured viscosities, values for the friction hindering molecular rotation, nevertheless such procedure does show that the expected temperature effect upon the dispersion ought to be considerable. As was to be expected the region of dispersion is pushed over towards the shorter wave lengths when an increase in temperature occurs, with its accompanying decrease in viscosity. Theory further predicts that in that region of wave-lengths in which the dielectric constant drops from its static value to its optical value, phase differences will be set up between the intensity of the active field and the polarization created. Now such phase differences are in general coupled with energy losses and we must, therefore, expect, for those same frequencies, the appearance of large absorption losses without any signs on the part of the insulator under examination, of conductivity in the ordinary sense. This also is found to be the fact.

Drude had already noticed this absorption experimentally, and, since then, the connection of the high-frequency losses with the polar character of the molecules and the viscosity of the liquid has been confirmed repeatedly. If we attach importance to very small high-frequency losses, then we ought to work only upon liquid insulators whose molecules are non-polar, such, for example, as benzene or carbontetrachloride.

A question which in recent years has been much worked upon is that of the connection between dipole-moments and chemical constitution. This connection may be illustrated and discussed by reference to some examples.

Monatomic molecules, like those of the "noble gases," are non-polar. Also, however, as symmetry demands, there is absence of polarity when two like atoms combine to form one molecule, as in O_2 or N_2. The case is different when two unlike atoms form a molecule. In this case it has been found possible, hitherto, always to establish the existence of a moment, namely a moment of very distinct magnitude, when the atoms, as in HCl, are very different, but quite small when, as in CO, the atoms are near together in the periodic system. A very beautiful example of the connection between the symmetry of the molecule and its polarity is provided by the series CH_4, CH_3Cl, CH_2Cl_2, CCl_4, examined by Sänger. Following the theory of van't Hoff we picture the two end members of this series as regular tetrahedra, and we do, in fact, find CH_4 and CCl_4 to possess zero moment, as the theory demands. The three intermediate molecules of the series are one-sided according to the structural formula, and exhibit that fact electrically by the presence of a dipole-moment. A further case, the characteristic meaning of which was pointed out long ago by J. J. Thomson (who, quite independently, but belatedly, reached also the dipole-theory) is that of benzene with two substitution atoms. Benzene itself (C_6H_6) is non-polar—agreeing well with the hexagonal chemical formula. If now we replace one hydrogen atom by chlorine we obtain the one-sided molecule of monochlorbenzene (C_6H_5Cl) and find it has a moment of 1.56×10^{-18}. The presumption now is that the distribution of electric charge which produces this moment must be actually very close to the C-Cl linking and that the more remote parts of the molecule have a comparatively unimportant bearing upon the polarity. If this is so, and if the benzene does possess the form of a regular hexagon, then it ought to be possible to predict the moments of the three isomers of dichlorbenzene. Assuming that there is no mutual action between the moments, all we need to do is to combine together, like forces, two moment vectors each of the magnitude 1.56×10^{-18}, setting them at 60° in the case of the ortho combination, at 120° for the meta and at 180° for the para. This is represented in Fig. 9, which gives also the measured moments (in units of 10^{-18}) and (in brackets) the values of the moments as calculated from the construction. The para combination has a zero moment, but this

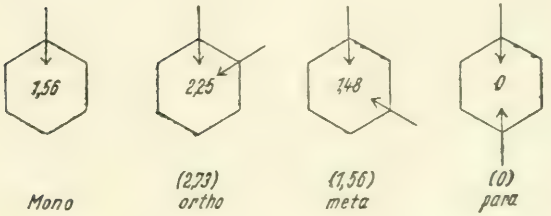

Fig. 9. Moments of the isomers of dichlorbenzene

is not because the parts of the molecule are individually nonpolar; it is rather because the two C-Cl moments balance out. The greatest discrepancy between the measured and the calculated values occurs with the ortho combination, the obvious reason being that, in this case, the C-Cl moments being closely adjacent, there is mutual interaction between them.

Another example in which the measurement of moments represents a valuable method of determining structure, is that of the cis-trans isomers. Errera finds the values given in Fig. 10 and thus establishes the notion that the trans-isomer is non polar. This agrees with the structural formula provided it be granted that the double linking between the carbon atoms fixes all the atoms of the molecule in one plane.

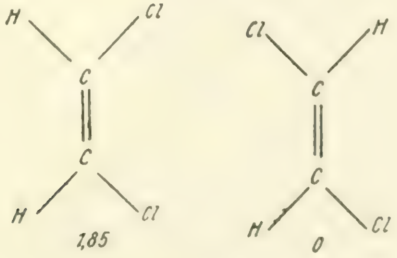

Fig. 10. Cis-trans isomers.

In the case of the pair of benzenes in which two like groups have been substituted in the para configuration, we find, in contrast to paradichlorbenzene, that the resultant moment is not always nil. Thus, for example, as Williams has shown, the substitution of two O-C_2H_5 groups in the para configuration instead of two H atoms, produces hydroquinone-diethylether with a moment of 1.75×10^{-18}. The explanation of this behavior must be sought in the fact that the two valency linkings going out from the O atom are mutually inclined at an angle. The moments of the groups possessing para configuration could then balance out only provided they were in opposition in space at every instant. Obviously, however, they are too far apart for this, and each group can, in fact, rotate independently of the other, as is suggested by Fig. 11.

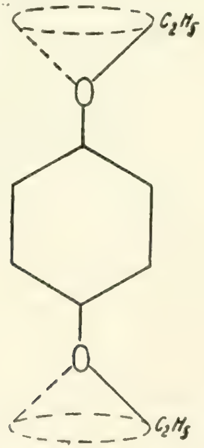

Fig. 11. Two groups in para configuration, mutually inclined, do not compensate.

The 180° angle between the valency linkings of the oxygen atom is frequently in evidence. A simple example is the water molecule, the value of whose moment (1.85×10^{-18}) makes it impossible for the three atoms to be in a straight line. The structure of the band spectra of water vapor shows that the H_2O molecule possesses three different moments of inertia. This confirms the conclusion drawn from the measurement of moments.

The structure of tri-atomic molecules is not always triangular. It is known without any doubt that the three atoms in the molecules CO_2 and CS_2 lie in a straight line—an arrangement which accords with the fact that they are non-polar.

As a final example we will discuss the peculiar behavior of dichlorethane. The formula shows only a single linking between the two carbon atoms,—a condition which, in stereochemistry, demands that the two halves of the molecule shall be capable of free rotation relatively to each other. The molecule does in fact possess a moment; hence the chlorine atoms are certainly not in the trans-configuration. It is, however, smaller than the moment which might be expected if the two halves of the molecule possessed truly "free" rotation. We have to conclude, therefore, from the measurements of moment, that a relative rotation of the groups does indeed occur, but we must note that this rotation is not completely "free," but favors the trans-configuration. Coupled with this should go the fact that the total moment is not constant, as, otherwise, it would be, but varies with temperature. This has been corroborated experimentally.

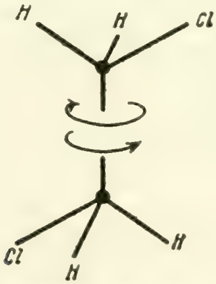

Fig. 12. Molecule with "free" rotation.

Up to this point I have spoken only of gases and liquids, and the inference might be drawn that "rotatable moments" *(drehbare Momente)* can hardly occur in solids. An electric moment is associated always with an atomic group, and, usually, we picture this group as so firmly anchored within the crystal structure that it is unable to make any movements except very small oscillations about its position of equilibrium. Recently, however, it has been shown by Pauling, that crystals may be conceived, easily, in which, at sufficiently high temperature, molecular groups may rotate to some extent "freely" without upsetting the crystalline structure. An example cited by Pauling is that of solid HCl. Cole, Dennison and Kemp have found a marked discontinuity to occur, at –175°C, in the values of the dielectric constant of solid HCl. This indicates that the HCl molecules, which, at lower temperatures, are polar and capable of rotation, become locked when this transition temperature is reached, and are subject no longer to rotations but only to oscillations.

The molecules in solids are very densely packed. Hence, when these molecules are polar, and are acted upon by an external field tending to line them up, the molecular electric fields of those among them which happen to be lined up already, will give considerable help to the applied external field. It is, indeed, conceivable that the molecular field may become so strong that, without the aid of any external field, and in spite of their thermal agitation, the molecules may become lined up to a considerable extent with their moments in one direction. In such a case that part of the body in which this process had occurred would become spontaneously polarized and we should have the electric analogy to a permanent magnet. According to Weiss we ought to think of a piece of iron, at ordinary temperature, as containing regions which are spontaneously magnetized. It is true that the mutual magnetic forces of the elementary magnets are much too small to cause this, but Weiss, at that time, assumed that in ferro-magnetic bodies there exists a molecular field of unknown origin which has the power to produce this lining-up. Recently this molecular field postulated by Weiss has found its explanation in a theory of Heisenberg, who attributes it to "forces of interchange" *(Austauschkräfte)* acting among the atoms—forces whose existence is demanded by the quantum theory. Ultimately these forces are electric and on this account possess the required magnitude, the mutual forces between electric "dipole-moments" being in any case great enough.

Thus the hope was warranted of discovering, within a practicable temperature range, an electric analogy to ferromagnetic substances. In 1921 Valasek did, in fact, disclose in Seignette salt (sodium potassium tartrate, the formula for which is $COONa\text{-}CHOH\text{-}CHOH\text{-}COOK+4H_2O$)* a crystal exhibiting electrically all of the peculiarities which, in iron, we observe magnetically. The matter was examined in particular by Kobeko and Kurtschatov. There is in that crystal a particular crystallographic direction along which, for weak fields very high values (greater than 1000) appear for the dielectric constant, and in which electric saturation *(Sättigung der elektrischen Polarisation)* is produced by fields of a few hundred volts per centimeter. The meaning we attach to this saturation is, as in the case of iron, that the axes of the spontaneously polarized regions have become lined up with the external field.

It is to be expected that this spontaneous polarization can exist only at sufficiently low temperatures. When the thermal agitation is great, the mutual electric forces no longer suffice to maintain the orderly arrangement. That is how Weiss explains the existence, in magnetism, of the "Curie point," that is to say the point of temperature (namely, 775 C for iron) at which a ferro-magnetic body loses its ferro-magnetic properties. "Seignette salt" should possess, therefore, a "Curie point" of polarization. It does in fact lose all evidences of saturation above 25.5C. For

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Translator's note: Rochelle salt.

temperatures below this there is complete analogy with the magnetic phenomena of hysteresis in iron. Which are the groups which suffer orientation within the crystal is not yet known definitely, but it seems highly probable that they are the water molecules, built, as these are, into the lattice as water of crystallization. It is possible, at any rate, to explain all the observed phenomena quantitatively by aid of disposable *(einstellbar)* moments of the ordinary order of magnitude of 10^{-18} electrostatic units.

THE MOLECULAR STRUCTURE OF LIQUIDS

The question of the structure of liquids was long regarded as solved by van der Waals' theory of the continuity of the gaseous and liquid states. According to this theory there is no fundamental difference between the two states regarded in the aggregate, a liquid being nothing more than a gas highly compressed. No externally applied pressure is required to hold it together, its liquid state being maintained by molecular cohesion which provides, automatically, a pressure of several hundreds of atmospheres. There is today no ground for doubting the soundness of this conception, but it leaves room for many questions designed to throw more light upon differences between the molecular states of gases and liquids. With this thought we may turn attention first to the condition of motion of the molecules. Afterwards the question may be surveyed whether there may not exist in liquids, on account of their great density, a tendency towards spatial arrangement foreshadowing that found in the crystalline state of solids. We shall concern ourselves in this lecture with experiments which elucidate both these points.

The experiments of Raman have shown that when molecules are illuminated with monochromatic light the energy-quantum *hn* of the impinging light may suffer change. The quantum may leave energy behind in the molecule, exciting this to oscillation or rotation, or possibly it may, in being scattered, carry energy away from the molecule. We shall not concern ourselves with the changes of frequency thus brought about. In the majority of cases the primary energy-quantum is sent out again without change. This ordinary scattering may be called "Rayleigh-scattering" to distinguish it from Raman-scattering, since it is to Lord Rayleigh, in his explanation of the blueness of the sky, that we owe the first discussion of the phenomenon of ordinary scattering.

We shall now consider the question—raised in the first instance for the case of a gas—whether the wave-length of the Rayleigh scattering is indeed strictly constant. Remembering that the speed of motion of the molecules in a gas is of the order of the speed of sound, that is to say a few hundred meters per second, we are led at once to expect wave-length changes due to the Doppler effect. If an observer should happen, for example, to be looking at a molecule along the direction of the incident light and this molecule should be, itself, retreating from the observer, then there are two reasons why the scattered light which goes to the observer must suffer change in wave length. First the fact that it is moving away from the light source causes the molecule to be excited with a frequency which is less than the primary light frequency seen by the observer. Then this reduced frequency which the molecule scatters suffers a second reduction, from the observer's point of view, because the molecule is retreating from the observer. Should the observer be looking in the opposite direction, that is to say towards the light source, then the two changes of frequency would be of opposite sign and the net result would be retention of the original frequency. When, therefore, we take into account the fact that all possible speeds and directions are represented within the gas, we must realize that a perfectly monochromatic primary beam must become spread out into a spectral line of finite width. The amount of this spreading must depend upon the angle between the line of observation and the primary beam. When looking in a direction not quite opposite to the primary beam, one must always observe a broadening of the spectral line. The intensity distribution in this broadened line represents the distribution of velocities among the gas molecules, while the breadth of the line increases as the direction of the line of observation comes more nearly into coincidence with the direction of the primary beam.

So far as I am aware, no investigation has yet been made of this effect. The opinion may indeed be held that such investigations—at any rate for gases—would be of no special interest, in view of the very definite knowledge we possess today, from many other sources, about the distribution of molecular velocities.

The position is different, however, when we consider the question how the light is affected when the scattering occurs in a liquid. Our knowledge of the conditions of motion of the molecules is by no means so good for liquids as for gases. In order to see, at the outset, whether there is reason to expect anything to occur characteristically different from what occurs in gases, it is appropriate to think first about solids and the way in which they produce scattering of light. They represent another limiting case *(Grenzfall)* which has been thoroughly mastered and which, —in spite of the fact that only gases and liquids exhibit continuity—may well be expected to show certain similarities to liquids.

As a concrete example let us take a crystal of rock-salt built up, in the well known way, of atoms of sodium and chlorine. The simplest picture we can make of the state of motion of these atoms is that which Einstein used in deriving his specific heat formula, a picture in which each atom swings about a position of equilibrium and is independent of its neighbors. If this picture were strictly right the deduction could easily be made—at any rate for high temperatures at which quantization has no noticeable effect—that the same spectral broadening of the primary light should occur as in a gas. We know, however, that this picture of the motion is too simple. Each atom is, in fact, so tied to its neighbors that its motion is not independent of the motion of the surrounding atoms. The actual condition is like the superposition of many different waves of sound, embracing a whole spectrum of frequencies, which traverse the body in all directions. I have used this notion before, in order to show that Einstein's specific heat formula ought to be replaced by another which gives, especially at low temperatures, a much slower decrease of specific heat with falling temperature (proportionality with the third power of the absolute temperature). We must ask ourselves whether this intercoupling of the motion of neighboring atoms may be of importance in the scattering of light. L. Brillouin stated and answered this question some years ago. He attributes the scattering, as did Einstein earlier, to the thermal changes in density and the consequent fluctuations of the refractive index. At the same time he takes into account the intercoupling of the fluctuations of neighboring regions by depicting the thermal agitation as a superposition of sound waves. In this way he finds for the scattering a result differing essentially from that which holds for gases. It may be formulated as follows:

If we consider the primary ray and a definitely directed scattering ray we conclude, first, that of all the possible "thermal heat waves" which traverse the body those only are of importance in sending "scatter-energy" in that particular direction, whose wave-front can be regarded as a mirror at the surface of which the ray is reflected, in the direction under consideration, according to the ordinary optical laws—in particular, the law of equality of the angle of incidence and reflection. There are very many waves with such fronts; waves differing in wave-length.

Next, as Brillouin has shown, the only waves, among those suitably directed, which are effective for the scattering process, are those having a quite definite wave-length. Those rays which come—by reflection—from surfaces separated by one whole wave-length, must be in phase. Only in that way can they co-operate so as to produce a noticeable scatter-intensity. This is analogous to the well known condition stated by Bragg for the reflection of Röntgen rays at the atom-planes of a crystal. In place of the Röntgen-ray wave-length, is the wave-length of light, and in place of the spacing of the atom-planes is the wave-length of sound waves. Thus from Brillouin's point of view the scatter-intensity in a given direction tells us in what strength thermal sound-waves of defined direction and wave-length are present in the body. Thermal sound waves of various directions and wave-lengths can be brought into action, in succession, by varying the direction along which the rays of scattered light are observed.

We know, however, that light reflected from a moving mirror suffers, by Doppler's principle, a change of wave-length. This principle holds also for the scattered light and its consideration leads us to a very interesting conclusion. There are actually two varieties of sound-waves present which are adapted, according to what we have said, to the scattering process; the one variety run upwards in Fig. 13, the other variety run downwards. The effect of the sound-waves going upwards is to raise the frequency of the primary light; the others will lower it. The order of magnitude of the changes in frequency is measured by the relation of the sound-velocity to light's velocity and depends, in addition (just as in the case of a gas, which we discussed above) upon the direction of observation. The characteristic thing is, however, that we ought to find not a broadening of the original spectral line but a splitting of it up into two sharp components.

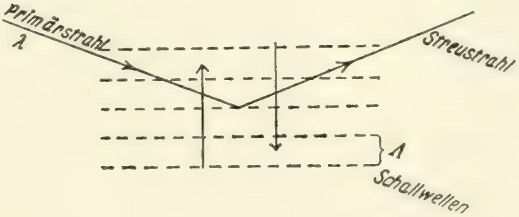

Fig. 13. Reflection by sound waves.

We are ready, now, to go on to the experiment with liquids. The question is whether a broadening or a splitting up of the original line accompanies the scattering. In the former event the thermal molecular motion of the liquid is like that in gases; in the latter event it is like that in a solid.

The earliest investigations of the fine structure of the spectral lines of Rayleigh scattering were made in Leningrad by Gross. He announced that it was possible by using an echelon grating to analyze the scattered light and obtain a photograph of the fine lines. He found, however, that there were several component lines, and this could not be explained. In addition it was stated by Rafalowski in Warsaw, who repeated Gross's experiments, that he could discover no splitting up of the primary spectral line. I, therefore, caused Meyer and Ramm to re-make the experiments in the Leipzig laboratory, using, first of all, as primary line the 4358A line of the quicksilver spectrum. These experiments, in which, also, an echelon grating was used, showed, at once, a splitting up, but only into a triplet of fine lines, not into a numerous group. The middle line of the triplet has the primary light's frequency; the two new component lines lie symmetrically to right and left. The results were not, however, as clear and definite as we wished. Toluol had been chosen as scattering liquid, and for this, separation between the middle line and the adjacent components is 0.06A. This is the same as the separation between the primary quicksilver line and several of its adjacent lines *(Trabanten)*. This fine-structure of the primary light naturally makes the meaning of the scatter-image unclear. Search was made, therefore, for some new source of light; a strong source being required because the scattered light, having had to traverse a monochromatic filter and also an echelon grating, has only a small fraction of the primary intensity. In addition the primary line should be single and free from adjacent components. These conditions were fulfilled by a quartz lamp filled with pure zinc. Such a lamp can be actuated in the same way as a quicksilver lamp but is more troublesome. The 4680A line of the zinc spectrum was used as primary light and with this the triplet formation, due to scattering, was very clear and unobstructed.

The wave-length separation of one of the side components from the middle line is 0.06A when the scattering is produced by means of toluol. The very same value, 0.06A, is obtained by calculation from the sound velocity. There is thus no question about it; we have here, exhibiting itself in a liquid, the effect which Brillouin predicted for solids, and we must conclude that thermal molecular motion takes place in liquids much as it does in solids. Each molecule is coupled strongly with its neighbors and we must picture the molecule as, for the most part, in oscillation. The oscillations cannot take place, however, as they do in solids, about a point which, on the average, is fixed; the mean center of oscillation must rather be one which wanders slowly through the liquid.

The generalization of this result would lead us to expect, for example, that the atomic-heat of a monatomic liquid must approach the Dulong and Petit value of 6 calories. This would be so because, now, the average potential energy of the oscillatory motion due to temperature rise would demand an influx of heat about equal to that which, in a gas, is the sole energy, namely, the kinetic energy—the amount of which is three calories per degree. This is confirmed in the case of liquid quicksilver, the atomic heat of which, at "constant volume" is 5.87 calories.

Exact agreement, however, does not exist between the experimental results obtained in liquids with scattered light and those calculated by Brillouin's theory. Calculation predicts not a triplet but a doublet—there ought to be no middle line. Experimentally this is far from being the case, and it does not seem possible to ascribe the presence of the undisplaced line to residual dust in the liquid. This component of the scattering may indeed result from the difference which undoubtedly must exist between the thermal agitation of a liquid and that of a solid. Another possibility is that the scattering which exhibits no change in frequency is an effect of fluctuations in the orientation of the molecules of the liquid. Such changes in orientation may make of the liquid a sort of aggregation of regions possessing crystalline properties—an aggregation in a state of continuous thermal agitation. At present neither experiment nor theory can decide between these alternatives.

At the end of his theoretical work Brillouin remarks that it would be very interesting, if it could be done, to test out his theory of the reflecting action of thermal sound waves by trial with sound waves produced artificially. On the occasion of a paper at the Massachusetts Institute of Technology in Cambridge (Mass.) on the subject of the experimental work of Meyer and Ramm, the same thought occurred to me, and I found in Sears a co-operator who was ready immediately to help to make the experiment. By aid of a high-frequency oscillator of quartz, ultra-sound waves, having a wave-length of a few tenths of a millimeter, were set up in a liquid. We tried, by adjusting the angle of reflection in accordance with Brillouin's theory, to cause light to be reflected at the wave front. Actually, however, interference phenomena began to appear immediately, before adjustment had been made. Concentrated by aid of a lens, the light coming out of the liquid produced upon a screen not only a central image of the slit which formed the light source, but also, to right and left, several spectra of considerable intensity, just as with an ordinary grating. Clearly, then, the periodic condensations and rarefactions set up in the liquid by the sound waves were playing the part of the ridges and grooves of a grating. Moreover, it is easily seen that the setting up of interference is unaffected by the fact that the sound-wave-grating sweeps across the lens with the speed of sound (say, one thousand meters per second). The effect is strongly visible; it can be seen readily upon the screen in a large auditorium. Very shortly after us, and quite independently, Lucas and Biquard announced the discovery of the same phenomenon.

Observation of the angular positions at which, when monochromatic light is used, the spectral lines appear which are thus set up by the sound waves, provides a very simple means of measuring both the speed of the sound and the compressibility of the liquid. I assume that this method, on account of its simplicity, will become important, as, for instance, in the measurement of the compressibility of liquified gases.

Although the theory of Brillouin does not explicitly predict the interference effects just described, but rather foresees only the reflexion referred to by Bragg, our results are not in conflict with that theory. If we take account of the fact that the dimensions of the volume traversed by the sound waves cannot be regarded as infinitely great compared with the wave-length of the light, the explanation follows from the same premises as are used by Brillouin. It is necessary, certainly, to go beyond the first approximation, by which the scattering is treated as a very small effect, for, otherwise, the appearance of spectra of higher order—so easily obtained—is inexplicable. The alternative possibility could not be substantiated, namely, that the quartz crystal sets up overtones of sufficient intensity.

Hitherto we have considered the fine structure of the scattered light in respect only of its wave length; there is, however, another structural characteristic, available to observation, which can give further information about the way in which liquids are built up. I mean the spatial structure, that is to say the distribution of the scatter intensity in different directions in space. Ordinary visible light discloses nothing of interest, the wave length being too great compared with the irregularities brought about by the molecular structure. It is necessary to use Röntgen light, with a wave length of about 1A ($= 10^{-8}$ cm.), and the question then before us is, what will be observed and what conclusions can be drawn from the observations?

The simplest case for observation is the scattering produced by a monatomic liquid, such, for example, as quicksilver. But even in this case it is necessary, first, to find out how a single atom of quicksilver scatters the primary Röntgen light. It is not, in fact, the heavy nucleus of the atom but rather it is the atom's shell of light electrons that is responsible for the scattering. The spatial dimensions of this shell are, however, of the order of 1A and so are comparable with the wave length being used. It comes about, therefore, that the different regions within an atom impart, through the scattering process, differences of phase to the light, and the observed intensity of scattering depicts an effect of the interference of the scattered rays which come from individual electron regions. The consequence is that an atom produces more forward scattering—that is to say scattering in the direction of the primary illumination—than backward. But the transition is shown by a smooth curve in which there are no preferred intermediate directions. This agrees both with calculation and with experiment. The experiment was made by Scherrer and Staeger,

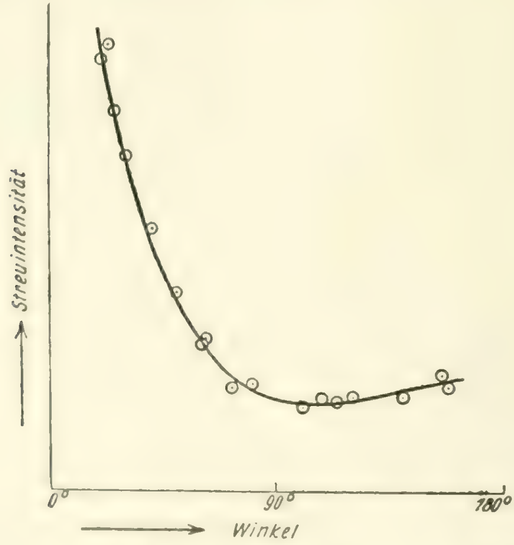

Fig. 11. Scattering by quicksilver vapor

who used the vapor of quicksilver. Fig. 14 gives the relation which was found between the scatter-intensity and the angle of scatter. In this figure the dots represent actual observations while the curve gives the result of calculation based on present knowledge of electron distribution within the atom.

Knowing now what the individual atom does, we experiment next with quicksilver in the liquid state. We allow the primary beam to strike the liquid surface at a small angle and then observe, say photographically, the secondary radiation which goes out in all directions from the spot on which the beam falls. And even if the primary beam penetrates only one-hundredth of a millimeter into the surface of the liquid, the result is characteristic of the liquid's inner structure. This is so because the surface peculiarities penetrate to a depth of only about one-millionth of a millimeter. The experiment was made in the Leipzig laboratory by Menke. Liquid quicksilver gives results quite different from those obtained with the gas, a complete series

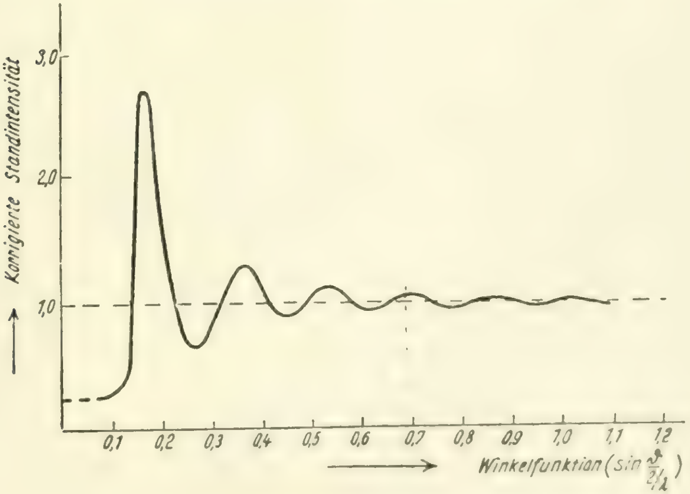

Fig. 15. Scattering by liquid quicksilver

of maxima occurring in the curve of intensity. And we know how to correct for the following disturbing influences, namely: the effect of absorption in the liquid; that of polarization—which always occurs in the process of scattering; and that of the falling off of intensity occasioned by the structure of individual atoms—an effect with which the gas experiment has acquainted us. What remains after these corrections have been made is a curve of intensity whose peculiarities depend chiefly on conditions characteristic of the arrangement of the atoms of the liquid. The results of such procedure are shown in Fig. 15, in which, again, for convenience, the function $(\mathrm{Sin}\vartheta/2)/\lambda$, instead of the angle ϑ is plotted along the axis of abscissae.

The curve of intensity shows marked maxima and minima and indicates, obviously, that in spite of the liquid condition with its greater freedom of movement of the quicksilver atoms, there is among these atoms a certain regularity of arrangement.

We wish now to consider in what way we ought to understand this regularity so as to deduce it from the experimental results.

Let us assume that we can actually see the atoms, and let us put our attention upon two of them, *A* and *B*. Locating ourselves on *A* so that we move with it, let us observe *B* continuously. In course of time *B* will approach *A*, possibly colliding with it: then it will recede. In short it will take up every possible position relatively to *A*. What we want to know is whether, among all the possible distances apart of *A* and *B* there are any which are preferred, or whether all of them are equally probable. We can obtain a clear and definite grasp of the problem by imagining that there belongs to *A* an element of volume—an element of volume located at an arbitrarily chosen but definite distance away from *A*—and observing for how long a time, during the wanderings of these two atoms, the middle point of *B* is located within that element of volume. By supposing this imagined experiment to be repeated for different distances between *A* and the element of volume, we obtain for each distance a certain time period which is proportional to the probability, for that distance, that *B* will be located within the assumed element of volume. If the curve could be drawn representing this probability as a function of the distance between *A* and *B*, it would provide us with actual quantitative information by which to describe the structure of the liquid.

We might try out the assumption that all distances are equally probable—excepting, of course, those very small distances which the atoms are unable to assume without interpenetration. When, however, the curve representing the probability as a function of the distance has been plotted definitely in accordance with any arbitrary assumption whatever, as, for instance, the assumption just named—it becomes possible, without any further hypotheses, to calculate the shape of the curve of scattering, that is to say the curve representing the (corrected) intensity of scattering as a function of the angle of scatter. When such a calculation is made under the assumption of equal probability for all distances a curve of scattering is obtained which is not at all like that (Fig. 15) given by actual observation. Instead of marked interference maxima there is only a very faint indication of such humps.

We must search for some other probability curve, so made that from it the observed distribution of intensity follows. Instead of searching, we may avail ourselves of a procedure, referred to by Prins and Zernike, which was first used by Menke. I have pointed out, already, that a knowledge of the curve of probability as a function of distance, makes possible the calculation of the curve of intensity as a function of angle of scatter. The converse of this holds, namely, that from a knowledge of the curve of scattering the probability curve can be deduced—use being made of an unambiguous mathematical procedure. This procedure was applied to the experimental results recorded in Fig. 15 and it produced Fig. 16. Here is an example of what Fig. 16 tells us: The two quicksilver atoms *A* and *B* have a marked preference for a mutual separation of 3.3A; they have also a preference, less marked, for a separation of 6A. In between lies a distance of 4.4A, which is avoided. Similar preferences are shown at greater distances, but the differences between successive preferences get less and less and finally vanish.

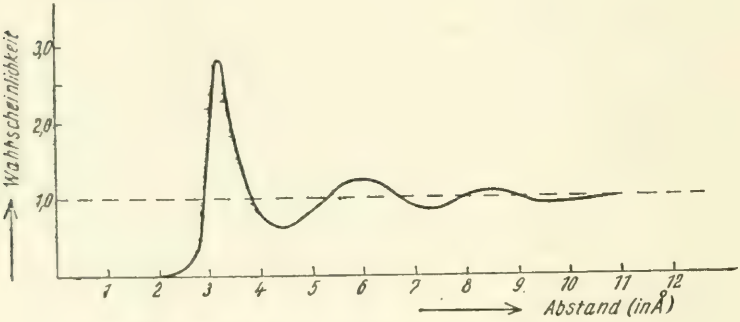

Fig. 16. Distribution of quicksilver atoms within the liquid.

In this preference for certain distances we find, undoubtedly, a close analogy with the crystalline structure of solids. The shape of the probability curve of Fig. 16 agrees quantitatively with the evidence found by von Laue and Bragg for the atomic framework of crystals.

The surprising nature of these results made us wish to study the phenomenon of preferred distances by means of a model. Upon the bottom of a box having a glass cover we laid a single layer of steel balls, some free space being left between the balls. Two of the balls were blackened. After the box had been shaken the distance between the two black balls was measured. This was repeated some 6000 times and from the figures obtained statistics were drawn up as to the frequency of occurrence of the different distances. The result was quite similar to that disclosed for a liquid by aid of scattered rays. The experiment with the model shows that there are preferred distances, and it provides a curve of distribution having the same general form as in Fig. 16. Prins has made a similar experiment: he used lycopodium, the distribution of which he observed by means of a microscope. He obtained corresponding results.

The case of the monatomic substance, quicksilver, is, undoubtedly, a very simple one. The case of a liquid made up not of atoms but of molecules is much more complicated. Interference maxima are set up by the action of the molecules themselves. Furthermore, characteristic waves of intensity variation are set up by the liquid, as such, on account not only of the spacing distribution but also, possibly, on account of orientation produced by mutual action between the molecules. Following upon the observation of interference phenomena in liquids—made first by Scherrer and later, in 1916, by me—the American investigator Stewart, in Iowa, has busied himself much with such experiments, and attaches great importance to the existence in liquids of molecular interactions tending to produce arrangement of the molecules. The fact that scattering in liquids is affected in an important way by interference effects of neighboring atoms, was first made clear by Keesom, who demonstrated the production of interference bands by the illumination of liquified monatomic gases.

Summarizing, we may say that experiments on the scattering produced by liquids have shown clearly, that in spite of the indisputable fact that the transition from the gaseous to the liquid state is a continuous one, the liquid state does show certain likeness to the solid state, the likeness concerning not only the condition of motion of the molecules but also their spatial arrangement.

THE STRUCTURE OF ELECTROLYTIC SOLUTIONS

The science of physical chemistry was erected, in the eighties of last century, upon the foundation of van't Hoff's work in applying the laws of gases to dilute solutions, Arrhenius's theory of dissociation, and W. Ostwald's application of the Guldberg Waage law to the determination of dissociation-equilibrium. A comprehensive understanding, both qualitative and quantitative, was soon obtained of the behavior of solutions. One group of substances, however, refused to fit into the frame of these fundamental laws—the so-called "strong electrolytes;" substances characterized by the fact that a large percentage of their molecules have become ionized. The difficulty appeared most clearly when the attempt was made to apply to these substances Ostwald's law of dilution. It is comparatively unimportant which phenomenon we may choose to consider. I shall take the lowering of the freezing point in order to demonstrate in what respect the results of experiment depart from the expectations of theory. We will assume that Fig. 17 represents the molar lowering of the freezing point as a function of the molar concentration—the expression "molar lowering of the freezing point" being taken to mean the quo-

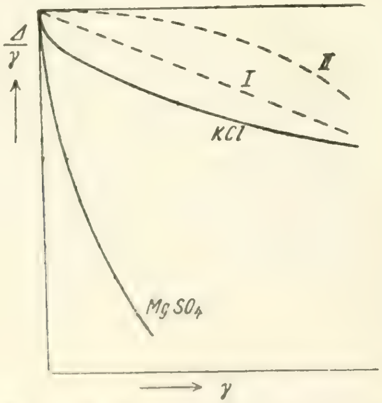

Fig. 17. Molar lowering of the freezing-point.

tient of the actual lowering, (delta), and the molar concentration, γ. According to van't Hoff's law the lowering of the freezing point is proportional to the number of free particles in unit volume. If we consider a salt such as KCl —completely ionized—we expect to find a lowering of the freezing point proportional to the concentration; but, in comparison with an undissociated substance, we expect a proportionality factor twice as great. Thus the molar lowering of the freezing point should be represented in the figure by a horizontal straight line. Actual experiment shows that the molar lowering falls off with increase of concentration. The explanation offered, in accordance with the classical law, was that, in strongly concentrated solutions, not all of the KCL molecules are ionized. Qualitatively that seems satisfactory, but difficulty arises as soon as the attempt is made, by aid of Ostwald's law, to express the degree of dissociation quantitatively. Confining our consideration first to a salt like KCl, which forms two ions, the Ostwald law says that for weak concentrations, the change of the degree of dissociation with concentration is proportional to the concentration. Thus we ought to expect a curve, like I in Fig. 17, which begins with a straight piece. If the salt splits into more than two ions, then it follows that more ions will meet when a molecule is formed, and this can occur less often than the collision of merely two ions. This state of affairs is expressed, according to Ostwald's law, by a curve which—if, for example, we take the case of a salt which splits into three ions—takes the shape II in the figure —a curve which departs but slowly from the straight line, namely, by an amount proportional to the square of the concentration.

Experiment shows, first of all, that the decrease in the molar lowering of the freezing point, with increase of concentration, is much greater than was expected, even for weak concentrations. This is indicated in Fig. 17 by the curves marked KCl and $MgSO_4$. It is found that, practically, the differences between the ordinates of the horizontal lines and those of the experimental curves, expressed by an exponential law, are proportional, for high dilution, to the square root of the concentration. Our first difficulty is that this square root law cannot be explained by mass action. A second difficulty is met by the classical theory when different uni-univalent salts of the KCl type are compared. Experiment shows that, with increasing dilution, the curves of molar lowering of the freezing point tend to coincide. From the standpoint of mass action this is not to be understood, for there is no apparent reason why the dissociation constants of different salts should be all alike. The behavior we are considering is brought to light still more characteristically by the case of salts which split into two ions, but into ions which carry a higher charge (often a double charge), as, for example, $MgSO_4$. In such cases a curve is obtained following a root law but falling more rapidly than in the case of the other salts. The decrease is still steeper in the case of ions having still higher valencies. It is thus not so much the number of ions that matters, but rather their valency. Lewis has expressed this quantitatively. According to him the properties of strong electrolytes in dilute solution are not expressible in terms of concentration as ordinarily understood. By a variation of the expression used by Sommerfeld for degree of freedom in the quantum theory the matter may be stated thus: "We must not only count the ions but also weigh them." What Lewis does is to multiply the concentration of each ion by the square of its valency and then to add together the different concentrations thus "weighted." He shows that this so-called "ion concentration" determines the properties.

Reviewing the experimental results, and comparing them with the classical laws, we see that, experimentally, the ionic charge plays an essential part, while on the other hand the magnitude of the ionic charge, as such, does not enter into the formulation of the classical laws. This disagreement has long been known, van Laar being one of the first to investigate it. Obviously, the fact ought to be taken properly into consideration, that ions, since they carry charges, exert mutual electrical forces and so, even when they are free, must affect the properties of the solutions. Milner has made the necessary calculation for the case of salts of the KCl type and has shown that the electrical forces are great enough to explain the observations. Although it is unwieldy, Milner's method of calculation is undoubtedly correct. Following after Milner, Ghosh tried to find a solution for all the problems by starting with a picture in which the distribution of the ions in a solution was exactly like that in a rock-salt crystal, with, however, the single difference, that the lattice constants were determined, in the solutions, by the concentration. Apart from the improbable nature of Ghosh's assumptions it is today agreed that his formulae fail to fit in with experimental results. It ought to be recognized, however, that the central idea in Ghosh's theory is good. When we consider, carefully, the way in which the forces between the ions can act—some ions carrying like charges, others carrying opposite charges—we are driven to the conclusion that the ions cannot be distributed throughout the space in complete disorder, but that their arrangement must exhibit, on the average, a certain structure. Qualitatively and quantitatively this structure can best be described in the following manner. We picture the distribution of the ions in, say, a KCl solution, as seen from the view-point of some particular K ion which, in imagination, we accompany in all its thermal movements. Putting attention, now, upon a small element of volume located at a fixed distance away from that K ion, we find that, in dilute solutions, it contains, usually, nothing but solvent, but sometimes it contains a K ion and at other times a Cl ion. Since, however, the K ions repel one another, while K and Cl ions mutually attract, it may naturally be expected that, on the average, the Cl ions will occupy that element of volume for a longer time than the K ions.

Thus for an averaged time period we may speak of a density of electricity in the region surrounding a central point at which there is a charge of opposite sign. This density, obviously, must be greater the smaller the distance from the central point. In this sense we say there is an "average ion cloud" which surrounds every ion, the spatial distribution of whose density indicates the structure set up in the solution by the ionic forces. The central problem has now become that of determining the distribution of the electricity in the ion cloud, for when this is known, the value of the free energy of the whole solution can be worked out easily and the thermodynamic behavior of the solution becomes known.

What is attained by such a theory is the remodelling of the laws of ideal dilute solutions, as formulated by van't Hoff, by aid of others which are found to apply to real solutions, in the same sense in which the remodelling of van der Waal's equation, by taking account of molecular forces, made it applicable to real gases instead of to ideal gases. There is, however, this difference, that with an ion solution —in contrast to a gas—the assumption is allowable that that part of the molecular forces which calls for consideration is known, since it consists only of the "Coulomb interaction" *(Coulombsche Wechselwirkung)* of the ions. This assumption brings with it, however, a difficulty. The Coulomb forces fall off comparatively slowly, namely, with the square of the distance. Hence it is not sufficient to take into account their forces of interaction only at moments when two ions come, by chance, into very close proximity. To do this, in respect of molecules, is permissible in deriving the equations for gases, but in solutions account ought to be taken of the coupling of each ion with all those in its neighborhood.

A simple procedure was found for determining the distribution of density in the ion cloud, the application of which enabled me, in co-operation with Hückel, to find an explanation for anomalous behavior of strong electrolytes. The square-root law is closely connected with the law of potential and so with the law of Coulomb. The importance of the quantity "ion strength," introduced by Lewis, lies in the fact that by its aid, the spatial extension *(Ausdehnung)* of the ion cloud is determined. The greater the ion strength the more closely does the ion cloud envelop the ions. In sufficiently dilute solutions the extension of the ion cloud is the only quantity of leading importance. It can be characterized by a length. We shall call this length the "radius" of the ion cloud. Its value, for water, is of the order of $10^{-8}\ \gamma^{1/2}$ cm., where γ is the concentration in mols per liter.

The fact that it has proved possible, at any rate in dilute solutions, to determine the conditions in a large number of cases, by simply observing the ionic forces, indicates that the degree of dissociation in these solutions is much nearer to 100% than we had been inclined, previously, to assume. Bjerrum, in particular, had long favored the view that the dissociation is complete, and the fact that, in all cases, the number of undissociated molecules in solutions of strong electrolytes must be quite small is borne out, not only by what we have said, but also by the negative results of recent experiments involving the Raman effect.

Hitherto we have brought into the discussion such phenomena only as conform, in a general way, with the principles of thermodynamics. New view-points arise when, along with processes that are reversible, we consider those which are irreversible, such, for example, as electrical conduction, diffusion, internal friction, etc. The conductivity of electrolytic solutions is of special importance, and it is significant that in this connection also the strong electrolytes exhibit peculiarities. If we plot the molar conductivity—defined as the actual conductivity κ divided by the molar concentration γ— as a function of the molar concentration, we find, as in the case of the molar lowering of the freezing-point, not the constant shown by a horizontal straight line, but a falling off with increase of concentration. Folowing classical theory we should be inclined to attribute this falling off—in accordance with Ostwald's law of dilution—to a reduction of the degree of dissociation. But we are prevented by difficulties similar to those met in the case of the lowering of the freezing-point. The law followed by the falling off of the molar conductivity is again a square-root law; the magnitude of the falling off being determined by the valency of the ions. This fact had already led Kohlrausch—to whom we are indebted for the square-root law of conductivity—to say that the variation of conductivity with concentration in strong electrolytes cannot be explained by the assumption of dissociation equilibrium. If we adhere, however, to the idea of almost complete dissociation in dilute solutions of strong electrolytes, our only way out is to attribute the decrease in conductivity to a decrease in the mobility of the ions. The problem before us, therefore, is to consider whether our ion cloud picture allows us to predict and to calculate such changes of mobility. It has in fact proved possible to explain, in this way, the Kohlrausch law, and to determine, quantitatively, the first part of the conductivity curve. In co-operation, again, with Hückel, I have made the necessary calculations—a final point of difficulty having been surmounted by Onsager. Two causes determine the increase in mobility

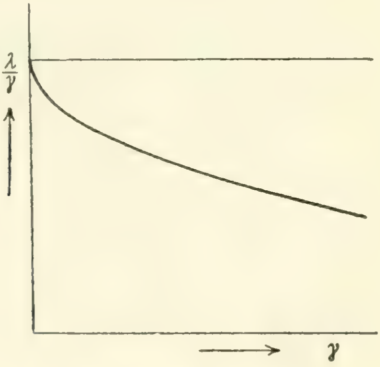

Fig. 18. Molar conductivity.

with increase of concentration: first, the Coulomb force *(Wechselwirkung)* of the ion changes with the surrounding solvent, and, second, an increase occurs in the interaction of the ions among themselves.

The first effect—known as the electrophoretic effect—depends particularly upon the existence of the ion cloud. For since, on the average, each ion is surrounded by a cloud carrying a charge of opposite sign, the solvent in the neighborhood of that cloud must be so acted on by the electric field which produces the current, that it tends to stream in the opposite direction. This streaming of the solvent must increase the friction acting on the ion, that is to say, must reduce the ion's mobility. A similar phenomenon can be produced on a large scale by applying an electrical difference of potential between the inside and the outside of a porous cell immersed in an electrolytic solution. The liquid streams through the cell wall because the water in the canals of the porous wall carries an excess of charge due to the varying degree of adsorption of oppositely charged ions on the material of the cell wall. This phenomenon, after which the effect has been named, is called electrophoresis

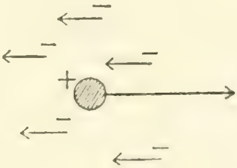

Fig. 19.

The second effect—known as the relaxation effect—depends on a change in structure suffered by the ion cloud on account of the passage of current through it, a change which results, further, from the fact that the cloud requires a certain finite time—the relaxation time—to come into existence or to disappear. If an ion were to be removed

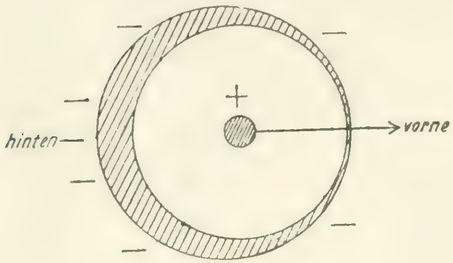

FIG. 20. Relaxation effect.

suddenly from an ion solution, a certain time would be required for the disappearance of the particular arrangement which had been created, in its own neighborhood, by that ion. The relaxation time characteristic of this process is, obviously, a new factor of essential importance in determining the ion cloud, and it must be considered along with the "radius" previously introduced. It is clear that in determining the relaxation time the mobility of the ions must be taken into account as well as the Coulomb forces. The greater the viscosity of the solvent and the smaller, on this account, the ionic mobility, the greater is the relaxation time. The order of magnitude of this quantity is, for water, 10^{-}[illegible] γ sec., where γ is the concentration in mols per liter. An increase in the concentration reduces the relaxation time; the separation of the ions becomes less, and the forces increase.

We will consider, say, a positive ion which is being moved to the right by an electric field. A continuous rebuilding of the ion cloud must occur in front of the movnig ion, a continuous collapse behind it. But, delayed by the relaxation time, the cloud in front will never attain its normal density of charge, while the density behind the ion will be permanently above normal. The consequence is an unsymmetry of charge distribution which exerts a purely electrical braking effect upon the ion, the ultimate effect being a further reduction in its mobility. The conditions are represented in Fig. 21. If the ions exerted no forces on one another the curve showing the relation between the molar conductivity, λ/γ, and the molar concentration, γ,

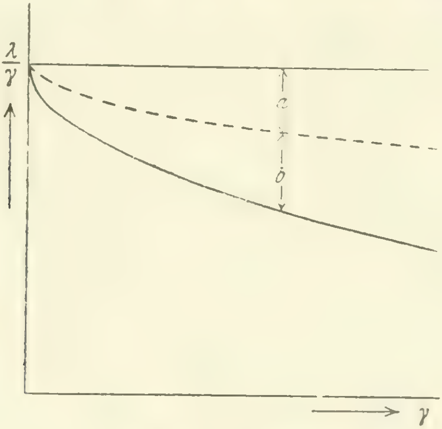

Fig. 21. Derivation of conductivity curve.

would be a horizontal straight line. The electrophoretic effect demands the subtraction of the amount a, the relaxation effect demands a further subtraction of the amount b, and since the influence of both these effects grows with the concentration—being proporional to the square root of the concentration—the resultant curve is as shown in the figure.

Up to this point we have confined our discussion to the explanation of long familiar experiments which, it appeared, could not be explained on the ground of dissociation equilibrium. One may ask whether it is not possible to think out new experiments the results of which will be directly characteristic of the theory of interionic attraction. A number of such experiments have, in fact, been made in recent years, in all of which the endeavor was to examine the behavior of solutions under extreme conditions.

First of all M. Wien showed that the conductivity of electrolytic solutions is increased by the presence of strong electric fields of the order of 10,000 to 100,000 volts per centimeter. The effect was discovered by Wien without reference to theory; later Joos and Blumentritt showed that the effect follows from modern theory.

After that came the prediction by myself and Falkenhagen that an increase in conductivity would be found if the measurement was made with high frequency current. This was proved true, experimentally, first by Sack and Brendel in Leipzig. It was corroborated later by various other investigators.

Thirdly, the fact was brought out during the same investigations, that the increase in conductivity was accompanied by an increase, due to the coupling of the ions, in the dielectric constant of the solution as compared with the pure solvent. This was first shown experimentally by M. Wien. Later it was corroborated by Jezewski and Kamecki.

Of these effects the simplest to explain is the second—the dispersion effect. Under the influence of an alternating field each ion in the solution moves back and forth. When the oscillations are slow enough, the unsymmetry of the distribution of charge in the ion cloud is as shown in Fig. 20—the central ion moving, meanwhile, to the right. While, however, it is moving to the left, the unsymmetry changes sign. But the ion cloud, in becoming unsymmetrical, requires a time of the same order as the relaxation time. If the central ion moves back and forth too quickly there will not be enough time for the setting up of the unsymmetry. But, in the absence of unsymmetry, there is no reason to subtract the quantity marked *b* in Fig. 21, that is to say, there is an increase in conductivity. Since, in water, the relaxation time is about $10^{-10}/\gamma$ second, we may expect the effect to be observable—using, for γ, a value of 0.001 mols per liter—with a periodic time of 10^{-7} second, that is to say for electrical waves having a wave length of 30 meters. The effect has, in fact, been shown with 30 meter waves. The dependence of the effect upon ionic valency as well as upon ion concentration and upon frequency has proved also to accord with expectation. The effect is particularly marked for ions of high value in solvents of high viscosity. Thus Gaertner, in Leipzig, using high frequency, found a six-fold increase in the conductivity of a solution of potassium ferrocyanide in a mixture of glycerine and water.

The Wien effect also can be demonstrated by aid of the properties of the ion cloud. If, for example, we employ a concentration of 0.01 mol per liter, the value of the radius of the ion cloud will be $r=10^{-8}/\gamma^{1/2}=10^{-7}$ cm. and the relaxation time will be $10^{-10}/\gamma=10^{-8}$ second. Thus an ion moving with a velocity of 10 cm. per second in the solution, would travel in the period of time necessary for the formation of its ion cloud a distance equal to the size of that cloud. Obviously, therefore, it would be unable to set up its cloud. But in the absence of the ion cloud neither the quantity a nor the quantity b of Fig. 21 ought to be subtracted, that is to say the conductivity must rise—reaching, in fact, the value corresponding to infinite dilution. The strong fields used by M. Wien produced an ion velocity of the order of one meter per second; it is thus evident why he found an increase in conductivity. It is to be expected that the valency of the ions must be of great importance. This is found to be the case, the Wien effect being particularly great with polyvalent ions. It is, further, to be expected that, with increase of field strength, the increase in conductivity will reach a limit, since its value cannot exceed that corresponding to infinite dilution. This also has been demonstrated, for sufficiently dilute solutions, by Wien.

Recently Wien has found that also weak electrolytes assume an increased conductivity under the influence of strong fields. This may be interpreted as a direct influence upon the degree of dissociation. Onsager tells me that such an interpretation of the effect is satisfactory provided we use the notion of ion pairs, as Bjerrum did,—pairs held together chiefly by their electrical forces.

Surveying the whole field here presented it seems to me impossible to avoid the conclusion that, in fact, the simple Coulomb effect *(Wechselwirkung)* of the ions is of essential practical importance.